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Muhammad Rizwan Latif
Boise State University

Maria Mitkova
Boise State University

Gary Tompa
Structured Materials Industries, Inc.

Elane Coleman
Structured Materials Industries, Inc.

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PECVD of Ge_xS_{1-x} Films For Nano-Ionic Redox Conductive Bridge Memristive Switch Memory

Muhammad Rizwan Latif, Maria Mitkova
Department of Electrical and Computer Engineering,
Boise State University
Boise, ID 83725, U.S.A.

Gary Tompa, Elane Coleman
Structured Materials Industries, Inc.
Piscataway, NJ 08854, U.S.A.

***Abstract*—This study is related to fabrication and characterization of redox conductive bridge memristors (RCBM). An active region in RCBM is formed by chalcogenide glass (ChG) doped with silver (Ag). We report the application of plasma enhanced chemical vapor deposition (PECVD) method for depositing ChG films which gives the advantage of flexibility in the composition and structure not easily achieved with sputtering or thermal evaporation. The growth kinetics of the deposition process, as well as the properties of the films is investigated. Optimal deposition conditions for reliable device performance are determined. The electrical characteristics of the devices fabricated at these conditions are also tested.**

Keywords—Redox conductive bridge memristors; chalcogenide glass; silver; solid electrolyte; film and device characterization

I. Introduction

Currently, flash memory is the most prosperous technology for non-volatile random access memory even though it possesses significant scaling challenges[1]. Among the new generation of non volatile memory that overcomes the scaling issue, Redox Conductive Bridge Memristor (RCBM) has attracted significant interest as a promising candidate for future high density, high performance memory and logic applications[2-4]. The nano-scaling attribute of memristors created a broad range of opportunities for low energy[5] and innovative memory architectures[6].

In RCBM, resistance change occurs in response to voltage flux by building up or dissolving a conductive molecular bridge between two electrodes. Conductive bridge is formed by electrochemical process within the solid electrolyte film sandwiched between an oxidizable metal electrode (anode) and an inert electrode (cathode) as shown in Figure 1. Solid electrolyte is formed by silver (Ag) diffusion in the chalcogenide (ChG) film. The device switches from a high resistive state (HRS) to a low resistive state (LRS) by the formation of a nano-scale conductive bridge created by the reduction of metal ions (SET State). A reverse bias dissolves the connection (RESET State)[7].

Common methods for ChG deposition in industrial facilities are either thermal evaporation or sputtering. Each of these methods has its own limitations; thermal evaporation does not allow compositional control whereas sputtering poses strict limitation on the composition of targets due to its mechanical requirements. The best solution to overcome these

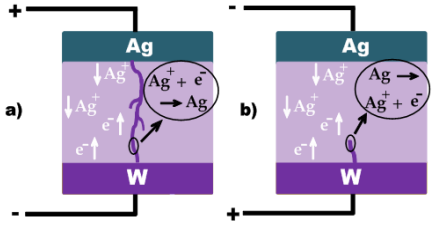

Figure 1 *a) Formation and b) dissolution of conductive bridge*

shortcomings is to use Plasma Enhanced Chemical Vapor Deposition (PECVD) which allows good control over the ChG composition in a dynamic environment. This method also offers good step coverage and depending on the deposition conditions, very relaxed Ge-S film structure can be achieved. The advantage of having control over ChG glass composition in the research mode is that it allows a wide range of material compositions to be evaluated for device optimization and in production allows one to readily compensate for any process drift.

In this work, studies related to Ge_xS_{1-x} films are presented which appears to be most reliable material for RCBM devices[8]. The deposited film structure, surface topography and composition were studied by Raman Spectroscopy, Atomic Force Microscopy (AFM) and Energy Dispersive X-Ray Spectroscopy (EDS) respectively. The devices fabricated by metal insulator metal stack (MIM) were electrically tested to show the applicability of the process for fabrication of RCBM.

II. EXPERIMENTAL DETAILS

The experiments were conducted using PECVD reactor with vapor drawn precursor delivery system and a RF plasma network. Small amounts of germanium (Ge) and sulfur (S) precursor vapors were injected into continuously flowing argon (Ar) stream. The vapor streams were then transported into the reactor chamber plasma. Precursors used for Ge and S were Germane (GeH_4) and Diisopropylsulfide ($C_6H_{14}S$) respectively. Ar was added as a reactant gas to the precursor mixture with a constant flow rate in the order of 500 SCCM (68% of the total gas flow). The pressure in the reaction chamber was maintained constant at 35-40Pa. The temperature of the substrate heater was varied from room temperature to 250°C with deposition time of 30 minutes. The net RF power (forward reflected) was 150 watts. The composition of Ge_xS_{1-x} system was dynamically controlled by controlling the gas precursors ratio along with the deposition temperature.

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The films were deposited on blank Si substrate as well as on stacks of SiO_2/W/TiO/SiO_2/Si for fabricating vertical devices. The thicknesses of the films comprising the devices were as follows: Si <100> substrate covered with 300nm thermally grown SiO_2; followed by 100nm of sputtered W and SiO_2 films. Ge-S films were deposited by PECVD method on patterned surfaces produced by using a 3in1 layered mask. Solid electrolyte was formed by fully saturating the Ag in the vias of vertical devices by photo-diffusion. It enables the fastest and the highest concentration of Ag incorporation in the ChG matrix compared to thermal diffusion process[9], thus reducing the post occurring effects of Ag ions during device switching. A UV collimated beam having an intensity of 0.5W/cm^2 was used for this purpose. For lateral devices Ag was deposited using shadow mask on stack of Ge-S/SiO_2/Si followed by thermal evaporation of Aluminum (Al) to form the inert electrode.

The chemical composition of the deposited films were determined using Hitachi S-3400N EDS system. EDS data was acquired by averaging data over five points on each sample. Raman spectra of the films were performed at room temperature in vacuum chamber using Horiba Jobin Yvon T64000 Raman spectroscopic system in back scattering mode. The Ge-S film surface characterization and stress analysis were studied by Bruker Dimensions 3100 AFM system.

Electrical testing on the devices was performed with Agilent 4155B Semiconductors Parameter Analyzer equipped with triax cables to avoid residual charge build up. W/Al and Ag pads were probed with correct biasing for SET and RESET conditions. The devices were tested in dual sweep mode with a voltage step size of 6mV with compliance current set to 700µA. Data were analyzed and recorded by Easy Expert Software provided by Agilent. All measurements were carried out at room temperature.

III. RESULTS

Table 1 summarizes EDS results of the films composition. The results confirm that with PECVD process, Ge_xS_{1-x} composition could be dynamically varied by controlling the gas precursors ratio and deposition temperatures. The deposited films are quite homogenous since EDS in different areas yielded a variation of ~1%. This is a key advantage of PECVD application for film deposition. It is observed that Ge composition decreases by decreasing the temperature, while keeping the deposition temperature same, an increase in the Ge:S gas precursor ratio results in increase in Ge composition in the film.

Table 1 EDS Data for different GeS Composition

Sample ID	Growing Temp (˚C)	Ge:S Precursor Ratio	Ge Atomic % by EDS	Thickness (nm)
Sample 1	250	7.0	59.47	370
Sample 2	200	7.0	35.45	115
Sample 3	150	7.0	34.55	276
Sample 4	150	10.1	37.40	177
Sample 5	120	7.0	36.83	175
Sample 6	120	10.1	49.57	116
Sample 7	100	8.6	34.52	187

The Raman study of the deposited films shows the presence of particular structural units corresponding to relaxed films. The observed spectra resemble the bulk material with same composition thus showing a low number of wrong chemical bonds. Raman spectra for PECVD deposited ChG films are presented in Figure 2. The results are consistent with already reported data[10]. The major Raman peak for S rich glasses is located at 340cm^{-1} which represents the breathing mode of $Ge(S_{0.5})_4$ corner sharing tetrahedra in which Ge is four fold coordinated and S is twofold coordinated. Its dominance fades with increasing the relative amount of Ge over 37 at.% when the edge sharing (ES) tetrahera, ethane-like structures and outrigger raft structure develop. This is special characteristic for the most Ge rich film (Sample 1) which is partially crystallized. Samples 3, 5 and 6 have the highest concentration of S. In them the presence of some S-S bonds at wave number 475 cm^{-1} and participation of corner sharing (CS) tetrahedral structure manifested by the breathing mode at 340 cm^{-1} are specifically illustrated on the Raman spectra.

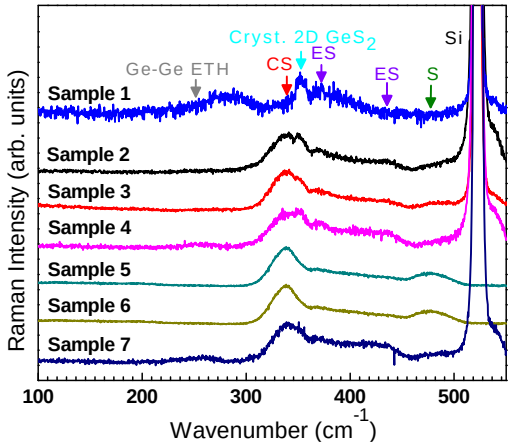

Figure 2. *Raman Analysis of PECVD deposited ChG films*

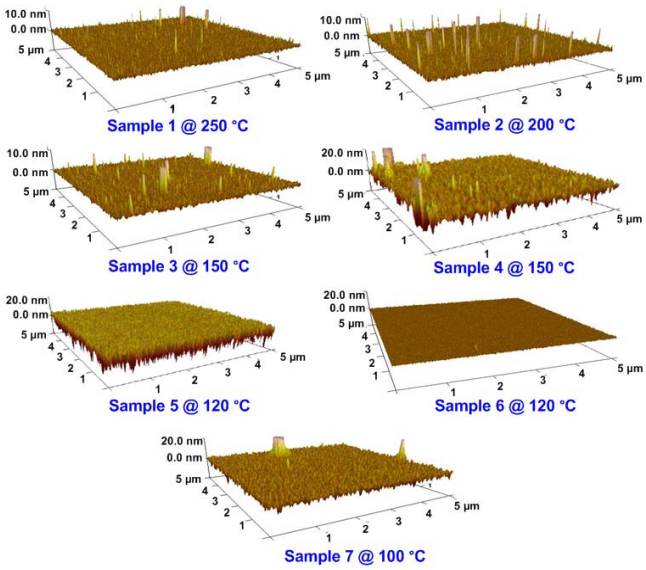

Figure 3. *AFM result for Ge_xS_{1-x} film deposition at different temperatures*

The AFM topography study shown in Figure 3 reveals that low temperature deposited films with relatively less concentration of Ge have good relaxed structure for accommodating high amount of Ag. Figure 4 shows the IV sweeps of the electrical measurements conducted on the fabricated lateral devices with composition corresponding to sample 5. The testing equipment (sample stage holder, triax cables and probes) was placed inside a faraday cage sharing a common ground to avoid static charge build up. Each cycle starts at -0.25V. Then the voltage sweeps to +1V and sweeps back to -0.25V. At first the current is very low (cell resistance: high) until a threshold voltage of approximately 0.65 V is exceeded. At that moment a conductive connection is formed between the top and bottom electrodes causing a steep increase in the current is observed until it reaches the compliance current limited to 700µA (cell resistance: low).

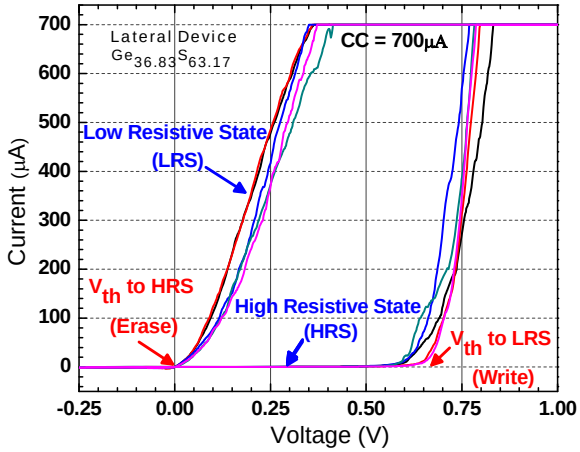

Figure 4. *IV curve of CVD deposited lateral devices*

IV. DISCUSSION

The most important result of this study is to establish a relationship between deposition conditions and film structure resulting in reliable device performance. The electrical testing was performed mainly on $Ge_{36.83}S_{63.17}$ which resulted in several hundred switching cycles. This composition was also favored, since corner sharing units are dominant structural units in it, as revealed by Raman peak area calculations shown in Figure 5. This gives high flexibility to the film structure. Although there are no published results related to the region of the intermediate phase[11] in this system, we suggest that these films could be related to it. The major feature of this phase is its thermodynamic stability[11] which in the aspect of studied devices means that their films do not age and their performance remains stable in time. Because of the higher connectivity, in difference to the stoichiometric composition GeS_2[10], there is no phase separation in this composition, as documented by the EDS studies.

With the deposition condition of sample 5 the structure appears to have relatively smooth surface with less frequency of hillocks, however in some cases hillock formations of up to 18nm are observed in the deposited films as presented in Figure 6. The surface roughness in thin films is very important factor for the system reliability[12, 13]. In RCBM device, the formation of conductive bridge is dependent on the distance between the two electrodes. Thus the statistical nature of the conductive filament growth process will be determined not by free available adsorption site at the electrode surface but by the closest distance between the electrode and hillock in the ChG layer[14]. This shows the importance of formation of smooth films. In our case smooth film surface was obtained at deposition temperature of 120ºC and pressure of 0.2-0.3 torr. This condition however, contradicts to some of the requirements for photolithography since the conventional photo resists (PR) are usually stable up to 115ºC.

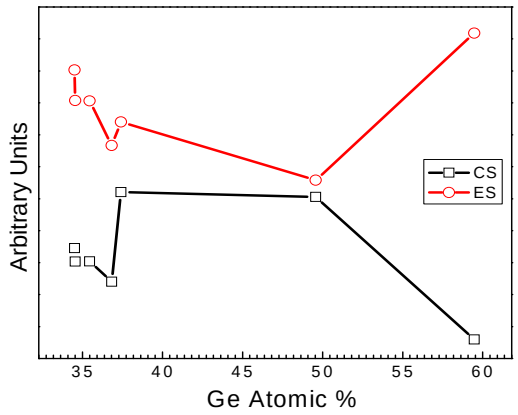

Figure 5. *Corner Sharing (CS), Edge Sharing (ES) and ES/CS trend with changing %Ge composition*

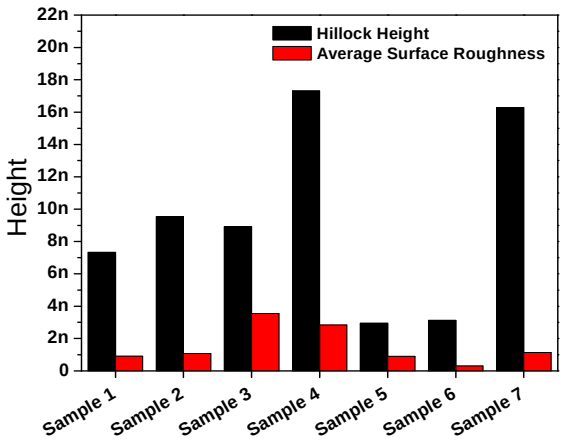

Figure 6. *Hillock formation and average surface roughness on the samples based on AFM scan of 5µm by 5µm area*

Figure 7 represents the resistance plot of the lateral device with dual sweep voltage. The plot shows four orders of magnitude difference between the ON and OFF state of the device. The resistance of the device varies from tens of mega ohms in the OFF state to few kilo ohms in the ON state ensuring good retention of devices[15]. The fact of the formation of a second plateau on the RV characteristic suggests dual growth of a conductive filament in the active film. For vertical devices with PECVD deposited Ge_xS_{1-x}

films, the lift off did not work well. The reason for this is unclear but we believe that PR reacts with sulphur radicals in the PECVD environment causing it to be non reactive to the micro-stripper solution. During the lift off of PR, the resist bonds needs to be broken to make PR soluble in the solvent. Another argument for the lack of efficiency of the lift off process is that in the PECVD method a slight increase in molecular weight of the resist may make it completely insoluble in the normal solvents. This can be due to the thermal cross-linking in case the reactor temperature is too high or the chemical reactions in the reactor are causing the molecular weight to increase.

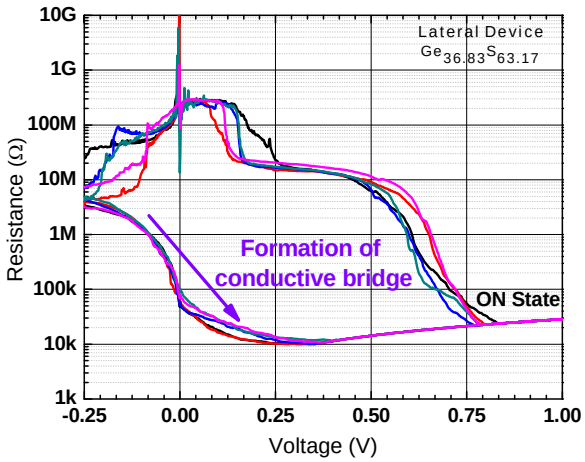

Figure 7. *Resistance vs Voltage Plot for lateral device*

V. CONCLUSION

Thin films of Ge_xS_{1-x} were produced by applying PECVD method and their composition was controlled in a dynamic environment. The obtained films are relaxed and their structure resembles the bulk glasses with same composition. High quality films for reliable performance of the RCBM devices are possible with this deposition method. Some compromises should be made in terms of application of relatively lower deposition temperatures which however results in surface with destroyed smoothness but at the same time could be very advantageous for the photolithographic process.

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REFERENCES

[1] D. Ielmini, A. S. Spinelli, and A. L. Lacaita, "Recent developments on Flash memory reliability," *Microelectronic Engineering*, vol. 80, pp. 321-328, 6/17/ 2005.

[2] L. Chua, "Memristor-The missing circuit element," *Circuit Theory, IEEE Transactions on*, vol. 18, pp. 507-519, 1971.

[3] J. R. Heath, P. J. Kuekes, G. S. Snider, and R. S. Williams, "A Defect-Tolerant Computer Architecture: Opportunities for Nanotechnology," *Science*, vol. 280, pp. 1716-1721, 1998.

[4] M. Hiroshi and O. Shunri, "Bottom-up approach to silicon nanoelectronics," *Microelectron. J.*, vol. 39, pp. 171-176, 2008.

[5] R. Waser, S. Menzel, and V. Rana, "Recent progress in redox-based resistive switching," in *Circuits and Systems (ISCAS), 2012 IEEE International Symposium on*, 2012, pp. 1596-1599.

[6] O. Kavehei, C. Kyoungrok, L. Sangjin, K. Sung-Jin, S. Al-Sarawi, D. Abbott, and K. Eshraghian, "Fabrication and modeling of Ag/TiO_2/ITO memristor," in *Circuits and Systems (MWSCAS), 2011 IEEE 54th International Midwest Symposium on*, 2011, pp. 1-4.

[7] R. Waser, R. Dittmann, G. Staikov, and K. Szot, "Redox-Based Resistive Switching Memories: Nanoionic Mechanisms, Prospects and Challenges," *Advanced Materials*, vol. 21, pp. 2632-2663, Jul 2009.

[8] R. Bruchhaus, R. Symanczyk, M. Kund, and M. Honal, "Selection of optimized materials for CBRAM based on HT-XRD and electrical test results," *J Electrochem Soc Journal of the Electrochemical Society*, vol. 156, pp. H729-H733, 2009.

[9] M. Mitkova, M. Kozicki, H. Kim, and T. Alford, "Local structure resulting from photo and thermal diffusion of Ag in Ge–Se thin films," *Journal of Non-Crystalline Solids*, vol. 338, pp. 552-556, 2004.

[10] M. Mitkova, Y. Sakaguchi, D. Tenne, S. K. Bhagat, and T. L. Alford, "Structural details of Ge-rich and silver-doped chalcogenide glasses for nanoionic nonvolatile memory," *Phys. Stat. Sol. A:Applications and Material Science*, vol. 207, pp. 621-626, 2010.

[11] P. Boolchand, D. Georgiev, and B. Goodman, "Discovery of the intermediate phase in chalcogenide glasses," *Journal of Optoelectronics and Advanced Materials*, vol. 3, pp. 703-720, 2001.

[12] H. Ji, G. S. Was, J. W. Jones, and N. R. Moody, "Effect of ion bombardment on in-plane texture, surface morphology, and microstructure of vapor deposited Nb thin films," *Journal of Applied Physics*, vol. 81, pp. 6754-6761, 05/15/ 1997.

[13] R. P. Vinci and J. J. Vlassak, "Mechanical Behavior of Thin Films," *Annual Review of Materials Science*, vol. 26, pp. 431-462, 1996.

[14] I. Valov and G. Staikov, "Nucleation and growth phenomena in nanosized electrochemical systems for resistive switching memories," *Journal of Solid State Electrochemistry*, pp. 1-7, 2012/10/01 2012.

[15] C. Kügeler, R. Rosezin, E. Linn, R. Bruchhaus, and R. Waser, "Materials, technologies, and circuit concepts for nanocrossbar-based bipolar RRAM," *Applied Physics A: Materials Science & Processing*, vol. 102, pp. 791-809, 2011.